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| <p>(21) International Application Number: PCT/GB99/04024</p> <p>(22) International Filing Date: 1 December 1999 (01.12.99)</p> <p>(30) Priority Data: 9826406.2 2 December 1998 (02.12.98) GB</p> <p>(71) Applicant (<i>for all designated States except US</i>): SOUTH BANK UNIVERSITY ENTERPRISES LTD. [GB/GB]; 103 Borough Road, London SE1 0AA (GB).</p> <p>(72) Inventor; and</p> <p>(75) Inventor/Applicant (<i>for US only</i>): KATHIRGAMANATHAN, Poopathy [GB/GB]; 14 Sandhurst Avenue, North Harrow, Middlesex HA2 7AP (GB).</p> <p>(74) Agent: COHEN, Alan, Nicol; 2 Grove Place, Tatsfield, Westerham, Kent TN16 2BB (GB).</p> | | <p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i></p> | |
| <p>(54) Title: ELECTROLUMINESCENT QUINOLATES</p> <p>(57) Abstract</p> <p>Lithium quinolate is an electroluminescent material which emits light in the blue region of the spectrum.</p> | | | |

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ELECTROLUMINESCENT QUINOLATES

The present invention relates to novel photoluminescent and electroluminescent materials.

5

Aluminium quinolate is a known photoluminescent and electroluminescent material and emits light in the red area of the spectrum. In order to obtain light of a different wavelength dopants and/or dyes have been added to the aluminium quinolate. Structures have also been made with a layer containing dyes in contact with the 10 aluminium quinolate layer but aluminium quinolate and structures based on aluminium quinolate have a relatively low efficiency.

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In an article by Takeo Wakimoto et al in Applied Surface Science 113/114(1997) 698-704 electroluminescent cells are disclosed in which aluminium quinolate is used 15 as the emitter and which is doped by quinacrodine derivatives which are fluorescent dyes to change the colour of the emitted light.

Electroluminescent devices can be made as described in an article by K. Nagayama et al in the Jpn. Journal of Applied Physics vol. 36 pps. 1555-1557.

20

The obtaining of blue light in an electroluminescent material is required to enable the complete range of colours to be obtained in devices incorporating such materials.

We have now obtained a novel electroluminescent material which emits blue light.

25

One aspect of the invention is lithium quinolate.

Another aspect of the invention is a method of making a metal quinolate which comprises reacting a metal alkyl or a metal alkoxide with 8-hydroxy quinoline.

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A further aspect of the invention is the provision of a structure which incorporates a layer of lithium quinolate and a means to pass an electric current through the lithium quinolate layer.

5 Although some metal quinolates are known hitherto lithium quinolate has not been made and it was surprising that it was photoluminescent and electroluminescent in the blue spectrum.

10 Aluminium and other known metal quinolates are made by the reaction of a metal salt with 8-hydroxyquinoline.

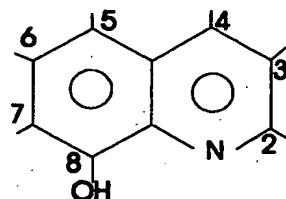
In the method of the invention the metal alkyl or alkoxide is preferably reacted in the liquid phase with the 8-hydroxyquinoline. The metal compound can be dissolved in an inert solvent added to the 8-hydroxyquinoline. The metal quinolate can be 15 separated by evaporation or when a film of the metal quinolate is required, by deposition onto a suitable substrate.

20 The preferred alkyls are ethyl, propyl and butyl with n-butyl being particularly preferred. With metal alkoxides the preferred alkoxides are ethoxide, propoxides and butoxides. The method is particularly suitable for the preparation of group I, II and III metals such as lithium, sodium, potassium, zinc, cadmium and aluminium alkoxides.

25 Lithium quinolate can be synthesised by the reaction, in an inert solvent, e.g. acetonitrile, of 8-hydroxyquinoline with a lithium alkyl e.g. n-butyl lithium. The lithium quinolate is an off white or white solid at room temperature.

As well as the lithium salt of 8-hydroxyquinoline, the term quinolate in this specification includes salts of substituted 8-hydroxyquinoline

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where the substituents are the same or different in the 2, 3, 4, 5, 6 and 7 positions and are selected from alky, alkoxy, aryl, aryloxy, sulphonic acids, esters, carboxylic acids, 5 amino and amido groups or are aromatic, polycyclic or heterocyclic groups.

Alkali metal alkyls are difficult compounds to handle practically as they are highly reactive and can catch fire spontaneously in air. For this reason they would not normally be chosen as reactants.

10

An electroluminescent device comprises a conductive substrate which acts as the anode, a layer of the electroluminescent material and a metal contact connected to the electroluminescent layer which acts as the cathode. When a current is passed through the electroluminescent layer, the layer emits light.

15

Preferably the electroluminescent devices of the invention comprise a transparent substrate, which is a conductive glass or plastic material which acts as the anode, preferred substrates are conductive glasses such as indium tin oxide coated glass, but any glass which is conductive or has a conductive layer can be used. Conductive 20 polymers and conductive polymer coated glass or plastics materials can also be used as the substrate. The lithium quinolate can be deposited on the substrate directly by evaporation from a solution in an organic solvent. Any solvent which dissolves the lithium quinolate can be used e.g. acetonitrile.

25 A preferred method of forming a metal quinolate film e.g. useful in

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electroluminescent devices comprises forming the metal quinolate in situ by sequential dip coating the substrate with the film e.g. the substrate is dipped or otherwise coated with a solution of the metal alkyl or alkoxide to form a film on the surface and then dipped or otherwise coated with 8-hydroxyquinoline or substituted 5 8-hydroxyquinoline and the metal quinolate film is formed on the substrate surface.

For example to form a film of lithium quinolate the film or layer of lithium quinolate is deposited by in situ dip coating i.e. the substrate, such as a glass slide, is dipped into or otherwise contacted with a solution of an alkyl lithium e.g. n-butyl lithium and 10 then immersed in or contacted with a solution of hydroxyquinoline, a layer of lithium quinolate is then formed on the substrate.

Alternatively the material can be deposited by spin coating or by vacuum deposition from the solid state e.g. by sputtering or any other conventional method can be used.

15 To form an electroluminescent device incorporating lithium quinolate as the emissive layer there can be a hole transporting layer deposited on the transparent substrate and the lithium quinolate is deposited on the hole transporting layer. The hole transporting layer serves to transport holes and to block the electrons, thus 20 preventing electrons from moving into the electrode without recombining with holes. The recombination of carriers therefore mainly takes place in the emitter layer.

Hole transporting layers are used in polymer electroluminescent devices and any of the known hole transporting materials in film form can be used.

25 The hole transporting layer can be made of a film of an aromatic amine complex such as poly(vinylcarbazole), N,N'-diphenyl-N,N'-bis (3-methylphenyl)-I,I'-biphenyl -4,4'-diamine (TPD), polyaniline etc.

30 Optionally dyes such as fluorescent laser dyes, luminescent laser dyes can be included

to modify the colour spectrum of the emitted light.

The lithium quinolate can be mixed with a polymeric material such as a polyolefin e.g. polyethylene, polypropylene etc. and preferably polystyrene. Preferred amounts 5 of active material in the mixture is from 95% to 5% by weight of active material and more preferably 25 to 20% by weight.

The hole transporting material can optionally be mixed with the lithium quinolate in a ratio of 5-95% of the lithium quinolate to 95 to 5% of the hole transporting 10 compound. In another embodiment of the invention there is a layer of an electron injecting material between the cathode and the lithium quinolate layer, this electron injecting layer is preferably a metal complex such as a different metal quinolate e.g. an aluminium quinolate which will transport electrons when an electric current is passed through it. Alternatively the electron injecting material can be mixed with the 15 lithium quinolate and co-deposited with it.

In another embodiment of the invention there is a layer of an electron transporting material between the cathode and the lithium quinolate layer, this electron transporting layer is preferably a metal complex such as a metal quinolate e.g. an 20 aluminium quinolate which will transport electrons when an electric current is passed through it. Alternatively the electron transporting material can be mixed with the lithium quinolate and co-deposited with it.

Optionally dyes such as fluorescent laser dyes, luminescent laser dyes can be included 25 to modify the colour spectrum of the emitted light and also enhance the photoluminescent and electroluminescent efficiencies.

In a preferred structure there is a substrate formed of a transparent conductive material which is the anode on which is successively deposited a hole transportation 30 layer, the lithium quinolate layer and an electron transporting layer which is

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connected to the anode. The anode can be any low work function metal e.g. aluminium, calcium, lithium, silver/magnesium alloys etc.

The invention is further described with reference to the examples.

5

Example 1 Lithium 8-hydroxyquinolate Li(C₉H₆ON)

2.32g (0.016 mole) of 8-hydroxyquinoline was dissolved in acetonitrile and 10ml of 1.6M n-butyl lithium (0.016 mole) was added. The solution was stirred at room 10 temperature for one hour and an off white precipitate filtered off. The precipitate was washed with water followed by acetonitrile and dried in vacuo. The solid was shown to be lithium quinolate.

Example 2 Lithium 8-hydroxyquinolate Li(C₉H₆ON)

15

A glass slide (Spectrosil UV grade) was dipped into a solution of n-butyl lithium in acetonitrile for four seconds and then immersed in a solution of 8 - hydroxyquinoline for four seconds. A thin layer of lithium quinolate was easily seen on the glass.

20

Example 3 Magnesium 8-hydroxyquinolate Mg (C₉H₆ON)₂

25 8-Hydroxyquinoline (5.0 -g; 0.0345 mole) was dissolved in 2N acetic acid (150 ml) by heating at 70 - 80°C. Magnesium sulphate (2.5 g; 0.020 mole) was dissolved in water (100 ml) heated to 60°C and basified with ammonia. Oxine solution was added to the mechanically stirred, basified magnesium sulphate solution at 60°C and excess ammonia added until the pH of the solution was 9.5. The yellow precipitate was digested at 60°C for a further 10 minutes, cooled and filtered under suction, washed with dilute ammonia and dried in vacuo at 100°C for several hours. Yield 5.06. g

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Example 4 Zinc 8-hydroxyquinolate Zn(C₂H₆ON)₂

The above procedure was employed using 8-hydroxyquinoline (5.0 g; 0.0345 mole) and zinc chloride (2.8 g; 0.020 mole). The yellow precipitate was filtered, washed 5 with dilute ammonia and dried in vacuo at 75°C for 6 hours. Yield 6.48 g

Example 5 Calcium 8-hydroxyquinolate Ca(C₂H₆ON)₂

Using similar procedure with 8-hydroxyquinoline (5.0 g; 0.0345 mole) and 10 calcium chloride (3.8 g; 0.034 mole), calcium 8-hydroxyquinolate was obtained as a yellow powder 5.60 g yield.

Example 6 Sodium 8-hydroxyquinolate Na(C₂H₆ON)

15 8-Hydroxyquinoline (5.0 g; 0.0345 mole) was dissolved in 2 % sodium hydroxide solution (100 ml) and heated to 60°C. The solution was stirred at this temperature for 30 minutes and the homogeneous solution was cooled to room temperature. No solid was separated out. Therefore the solution was concentrated in a rotary evaporator and the concentrated solution was cooled to give a 20 pale yellow solid. The solid was filtered under suction washed with small amounts of sodium hydroxide solution and dried in vacuo at 80°C for several hours. The sodium 8-hydroxyquinolate is soluble in water. Yield 3.6 g.

Example 7 Potassium 8-hydroxyquinolate K(C₂H₆ON)

25 Potassium 8-hydroxyquinolate was also made from 8-hydroxyquinoline (2.0 g; 0.0138 mole) in dry tetrahydrofuran (50 ml) and potassium tert-butoxide (2.32 g; 0.021 mole). The solution was heated to become homogeneous and cooled to room temperature to give a yellow solid yield 2.2 g.

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The photoluminescent efficiency and maximum wavelength of the PL emission of the lithium quinolate was measured and compared with other metal quinolates and the results shown in Table 1. Photoluminescence was excited using 325nm line of Liconix 4207 NB, He/Cd laser. The laser power incident at the sample (0.3mWcm⁻²) was measured by a Liconix 55PM laser power meter. The radiance calibration was carried out using Bentham radiance standard (Bentham SRS8, Lamp current 4,000A), calibrated by National Physical laboratories, England. The PL studies were carried out on samples or films. The Spectra are attached as Figs. 2 to 7.

10

Table 1

| | | | Absolute Photoluminescent Efficiency % | |
|----|------------------|------------|--|-------------|
| | Complex | CIE x,y | λ_{max} (PL)/nm | η_{PL} |
| 15 | Li _q | 0.17, 0.23 | 465 | 48 |
| | Na _q | 0.19, 0.31 | 484 | 32 |
| | K _q | 0.19, 0.33 | 485 | 36 |
| | Ba _{q2} | 0.16, 0.29 | 479 | 7 |
| | Ca _{q2} | 0.21, 0.37 | 482 | 24 |
| 20 | Mg _{q2} | 0.22, 0.46 | 500 | 43 |
| | Zn _{q2} | 0.26, 0.51 | 518 | |
| | Al _{q3} | 0.32, 0.56 | 522 | 27 |

Example 8

25

An electroluminescent device of structure shown in fig. 1 was fabricated using aluminium quinolate and lithium quinolate as the electroluminescent layer and the electroluminescent properties measured. Referring to fig. 1 (2) is an ITO layer, (4) is a TPD layer (hole transporting layer) (60nm), (1) is the lithium quinolate layer (5) is an aluminium quinolate layer and (3) is aluminium (900nm).

30

1. Device Fabrication

An ITO coated glass piece ($1 \times 1\text{cm}^2$ cut from large sheets purchased from Balzers, Switzerland) had a portion etched out with concentrated hydrochloric acid to remove 5 the ITO and was cleaned and placed on a spin coater (CPS 10 BM, Semitec, Germany) and spun at 2000 rpm for 30 seconds, during which time the solution of the electroluminescent compound was dropped onto it dropwise by a pipette.

Alternatively the electroluminescent compound was vacuum evaporated onto the ITO 10 coated glass piece by placing the substrate in a vacuum coater and evaporating the electroluminescent compound at 10^{-5} to 10^{-6} torr onto the substrate.

The organic coating on the portion which had been etched with the concentrated hydrochloric acid was wiped with a cotton bud.

15 The coated electrodes were stored in a vacuum desiccator over calcium sulphate until they were loaded into a vacuum coater (Edwards, 10^{-6} torr) and aluminium top contacts made. The active area of the LED's was 0.08 cm^2 by 0.1 cm^2 the devices were then kept in a vacuum desiccator until the electroluminescence studies were 20 performed.

The ITO electrode was always connected to the positive terminal. The current vs. voltage studies were carried out on a computer controlled Keithly 2400 source meter.

25 Electroluminescence spectra were recorded by means of a computer controlled charge coupled device on Insta Spec photodiode array system model 77112 (Oriel Co. Surrey, England)

30 The spectra are shown in the drawings.

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In the spectra:-

Fig. 2 shows the PL of lithium 8-hydroxyquinolate of Example 1 and the quinolates of Examples 6 and 7.

5 Fig. 3 shows the PL of quinolates of Examples 3 and 5 and that of barium quinolate made by the same method.

Fig. 4 shows the PL of zinc quinolate of Example 4

Fig. 5 shows the PL of commercially available aluminium quinolate and

Fig. 6 shows the UV-VIS, PL and EL of lithium quinolate and

10 Fig. 7 shows the spectra of lithium quinolate of Example 2

Claims

1. Lithium quinolate.
- 5 2. A method of making lithium quinolate which comprises reacting a lithium alkyl or alkoxide with 8-hydroxy quinoline or substituted 8-hydroxy quinoline.
- 10 3. A method of making lithium quinolate as claimed in claim 2 in which a lithium alkyl or alkoxide is reacted with the 8-hydroxyquinoline in the liquid phase.
- 15 4. A method of making lithium quinolate as claimed in claim 3 in which a film of lithium quinolate is deposited onto a substrate.
5. A method as claimed in claim 4 in which the substrate is dipped or otherwise coated with a solution of the lithium alkyl or alkoxide to form a film on the surface and then dipped or otherwise coated with 8-hydroxyquinoline and the lithium quinolate film is formed on the substrate surface.
- 20 6. A method as claimed in any one of claims 2 to 5 in which the alkyl is ethyl, propyl or butyl.
7. A method as claimed in any one of claims 2 to 5 in which the metal alkoxide is an ethoxide, propoxide or a butoxide.
- 25 9. A structure which incorporates a layer of lithium quinolate and a means to pass an electric current through the lithium quinolate layer.
10. An electroluminescent device comprises a conductive substrate which acts as the anode, a lithium quinolate layer and a metal contact connected to the electroluminescent layer which acts as the cathode.

11. An electroluminescent device as claimed in claim 10 in which the substrate is transparent conductive glass or plastic material.
- 5 12. An electroluminescent device as claimed in claim 11 in which there is a hole transporting layer deposited on the transparent substrate and the lithium quinolate is deposited on the hole transporting layer.
- 10 13. An electroluminescent device as claimed in claim 12 in which the hole transporting layer is made of a film of poly(vinylcarbazole), N,N'-diphenyl-N,N'-bis(3-methylphenyl)-I,I'-biphenyl -4,4'-diamine (TPD), polyaniline.
14. An electroluminescent device as claimed in any one of claims 10 to 12 in which a dye is included to modify the colour spectrum of the emitted light.
- 15 15. An electroluminescent device as claimed in any one of claims 10 to 14 in which the lithium quinolate is mixed with a polyolefin and the amount of lithium quinolate in the mixture is from 95% to 5% by weight of the mixture.
- 20 16. An electroluminescent device as claimed in claim 16 in which the amount of lithium quinolate is from 25 to 20% by weight of the mixture.
- 25 17. An electroluminescent device as claimed in any one of claims 12 to 16 in which a hole transporting material is mixed with the lithium quinolate in a ratio of 5-95% by weight of the lithium quinolate to 95 to 5% by weight of the hole transporting compound.
- 30 18. An electroluminescent device as claimed in any one of claims 12 to 17 in which there is a layer of an electron injecting material between the cathode and the lithium quinolate layer,

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19. An electroluminescent device as claimed in any one of claims 12 to 17 in which there is an electron injecting layer mixed with the lithium quinolate
- 5 20. An electroluminescent device as claimed in claim 18 in which the electron injecting layer is a different metal quinolate which will transport electrons when an electric current is passed through it.
- 10 21. An electroluminescent device as claimed in claim 18 in which the electron injecting layer is aluminium quinolate
- 15 22. An electroluminescent device as claimed in claim 12 in which there is a substrate formed of a transparent conductive material which is the anode on which is successively deposited a hole transportation layer, the lithium quinolate layer and an electron transporting layer which is connected to a metal anode.

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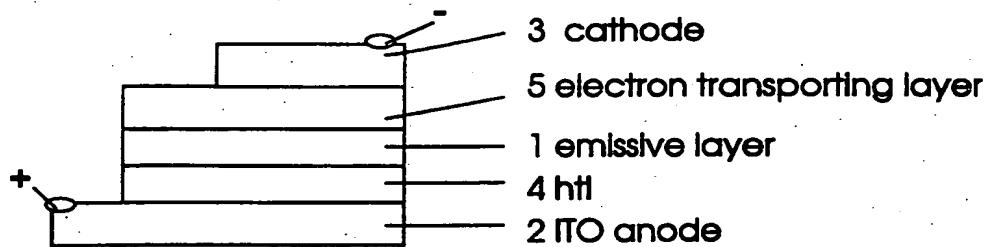


Fig. 1

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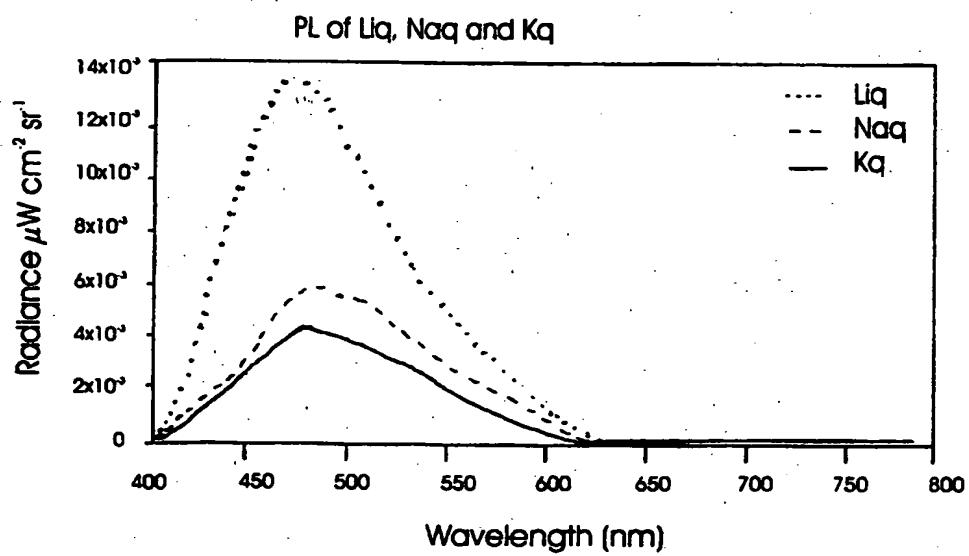


Fig. 2

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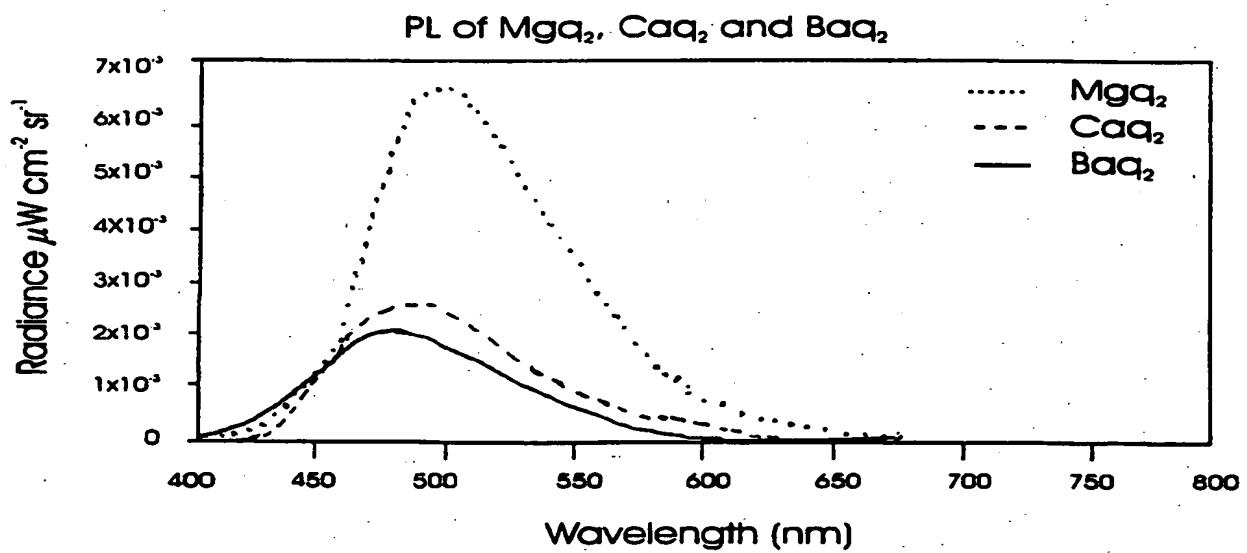


Fig. 3

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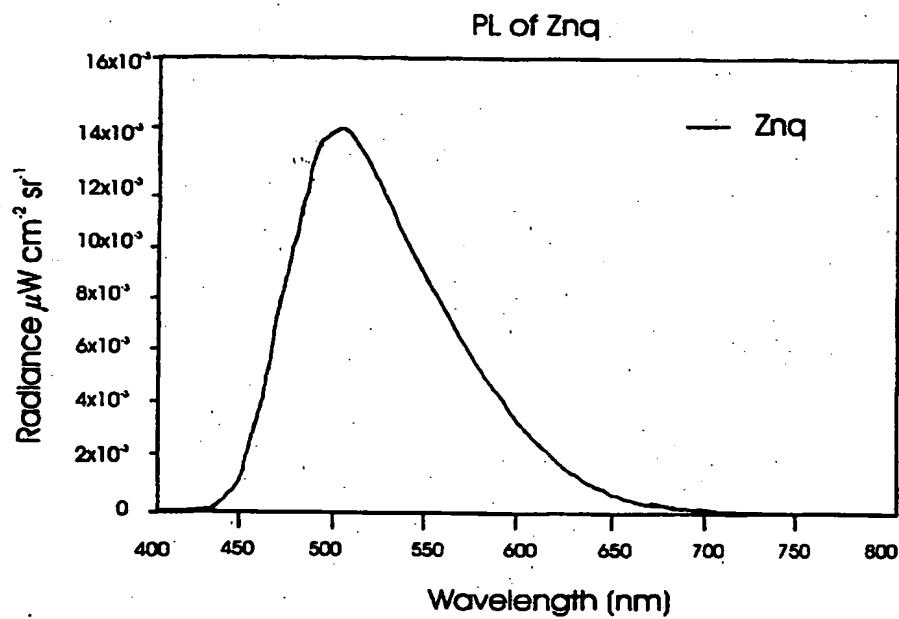


Fig. 4

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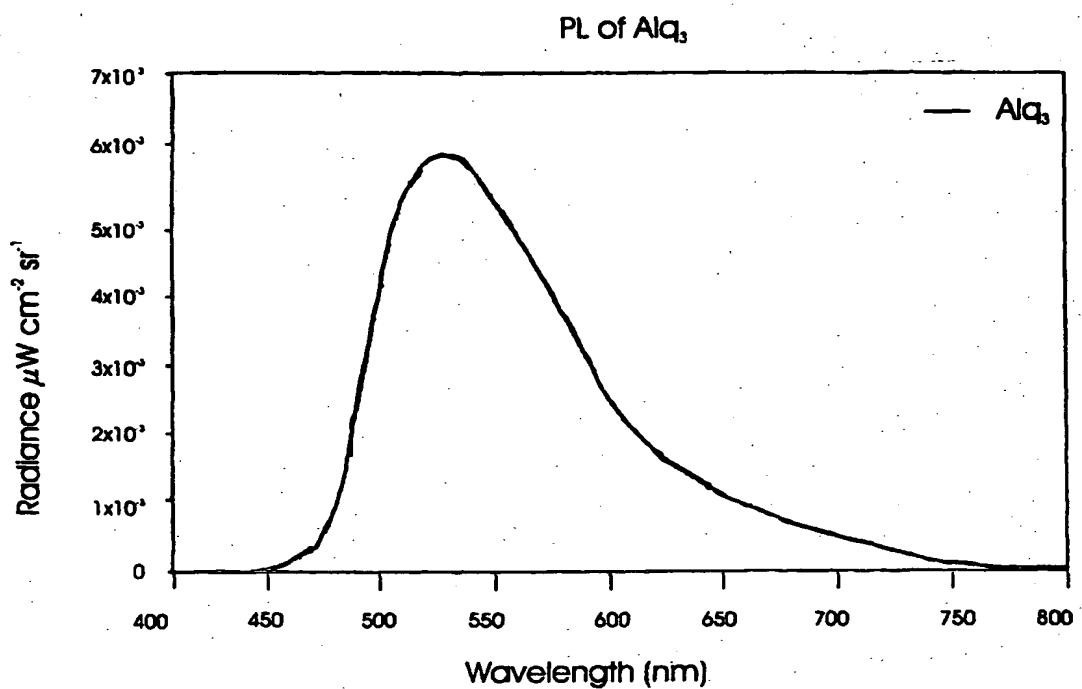


Fig. 5

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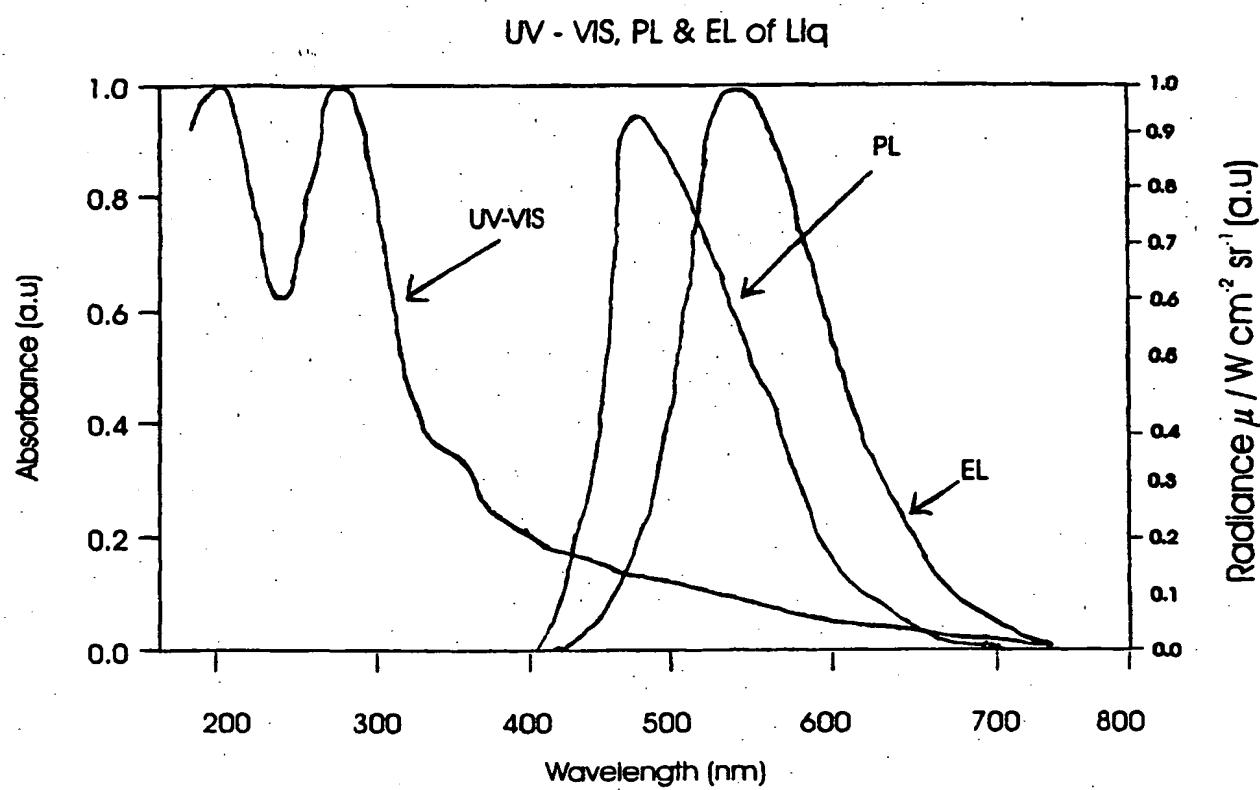


Fig. 6

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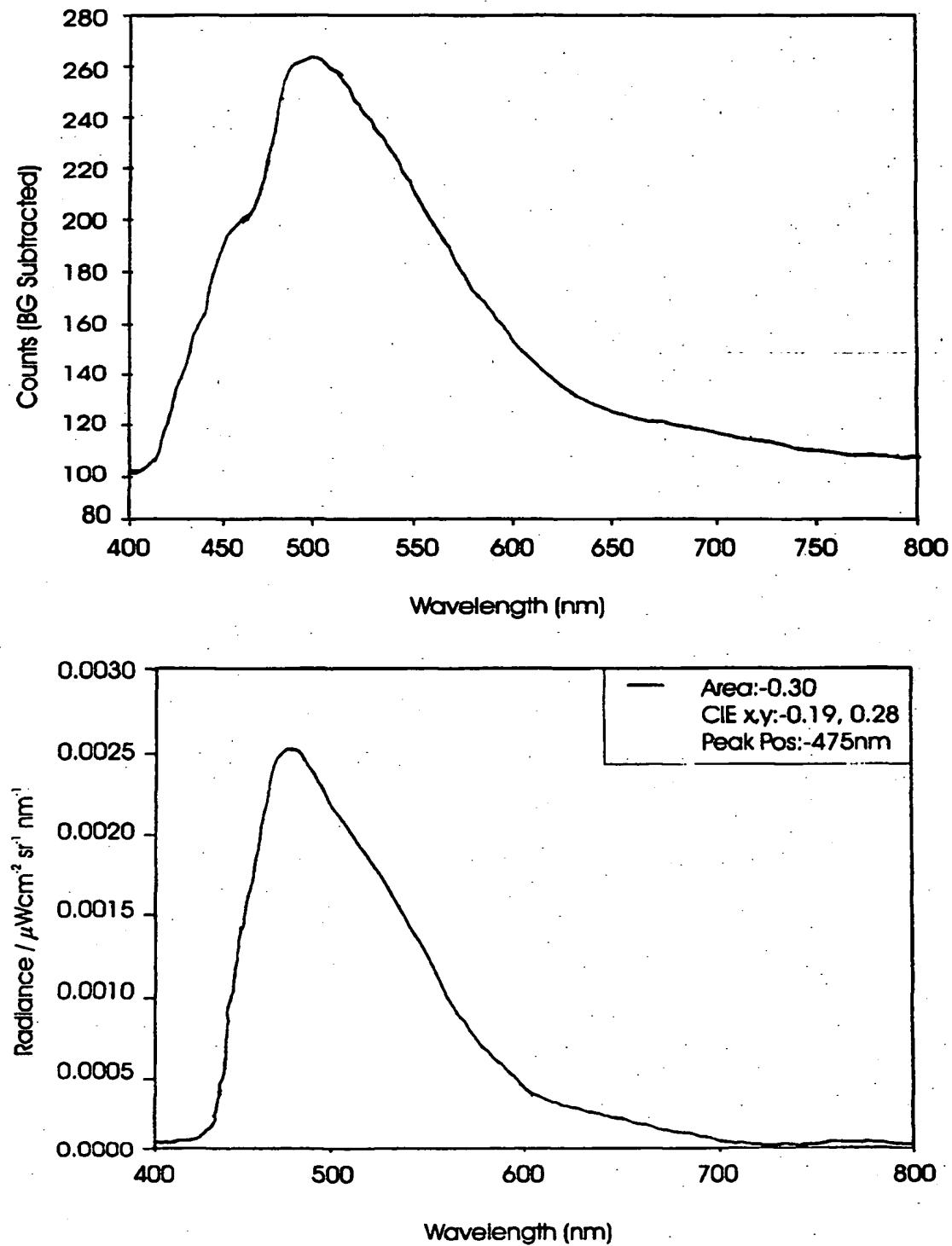


FIG. 7

INTERNATIONAL SEARCH REPORT

Inten. Appl. No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09K11/06 H05B33/14 C07D215/30

According to International Patent Classification (IPC) or to both national classification and IPC

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|----------|--|-----------------------|
| X | HENSEN, KARL ET AL: "Preparation of N- or 0-chloromethylsilyl derivatives of amines 1,2,3,4-tetrahydro-1,10-phenanthroline and 8-hydroxyquinoline" J. ORGANOMET. CHEM. (1981), 209(1), 17-23 , XP002130687 page 21, paragraph 4 | 1-3,6,7 |
| P, X | EP 0 936 844 A (KIDO JUNJI ;INT MANUFACTURING AND ENGINEER (JP)) 18 August 1999 (1999-08-18) example 1 | 1,9-11 |
| X | WO 98 02018 A (BAYER AG ;BOSCH GMBH ROBERT (DE); WEHRMANN ROLF (DE); ELSCHNER AND) 15 January 1998 (1998-01-15) the whole document | 1,9-22 |
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Patent family members are listed in annex.

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Date of the actual completion of the International search

28 February 2000

Date of mailing of the International search report

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| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT | | |
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| X | US 5 755 999 A (CHEN CHIN H ET AL) 26 May 1998 (1998-05-26) column 35, line 19 — | 1,9-22 |
| X | EP 0 569 827 A (IDEMITSU KOSAN CO) 18 November 1993 (1993-11-18) page 19, line 31 — | 1,9,10 |
| A | PATENT ABSTRACTS OF JAPAN vol. 018, no. 462 (C-1243), 29 August 1994 (1994-08-29) & JP 06 145146 A (CHISSO CORP), 24 May 1994 (1994-05-24) abstract — | 1,9,10 |

INTERNATIONAL SEARCH REPORT
Information on patent family members

International Application No
PCT/GB 99/04024

| Patent document cited in search report | Publication date | Patent family member(s) | | Publication date |
|--|------------------|-------------------------|------------|------------------|
| EP 0936844 A | 18-08-1999 | JP | 11233262 A | 27-08-1999 |
| WO 9802018 A | 15-01-1998 | DE | 19627070 A | 08-01-1998 |
| | | AU | 3692497 A | 02-02-1998 |
| | | EP | 0910930 A | 28-04-1999 |
| US 5755999 A | 26-05-1998 | EP | 0878529 A | 18-11-1998 |
| | | JP | 10330744 A | 15-12-1998 |
| EP 0569827 A | 18-11-1993 | JP | 6313168 A | 08-11-1994 |
| | | US | 5516577 A | 14-05-1996 |
| JP 06145146 A | 24-05-1994 | NONE | | |